

Theoretical Essay on the Distribution of Energy in the Spectra of Solids ⁽¹⁾

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⁽¹⁾ Summary of an article recently published in the *Journal of the Russian Physico-Chemical Society*, vol. XIX, no. 4, p. 79; 1887.

The latest remarkable publications of Mr. Langley on invisible spectra ⁽²⁾ and especially the promise of a special Memoir on the radiations of solids at different temperatures, encourage me to publish, from now on, at least in abbreviated form, some theoretical considerations on this subject. I hope to give a more complete discussion of the question when new data from the spectro-bolometric research of Mr. Langley will enable me to compare my theory with experiment in a more detailed manner.

⁽²⁾ S.-P. Langley, *On Invisible Spectra* (*Ann. de Ch. et de Phys.*, December 1886, pp. 433–506). See also *Amer. Journ. of Sc.*, vol. XXXII, Aug. 1886, as well as *Phil. Mag.*, vol. XXI, pp. 394–409, and vol. XXII, pp. 149–173.

1. Hypotheses and General Law

The absolute continuity of spectra emitted by solids can only be explained by a complete irregularity of the vibrations of their atoms. The discussion of the distribution of radiant energy among simple radiations of different period therefore falls within the domain of the calculus of probabilities.

Let us consider a homogeneous isotropic solid, in which all the atoms are in identical conditions, no longer grouped, so to speak, into distinct molecules. Each atom has a fixed equilibrium position toward which it is constantly pushed back by the surrounding atoms and around which it describes infinitely small oscillations. I express this fact by supposing that each atom moves freely within an elastic spherical shell of infinitely small radius r , whose center is the equilibrium position. The atom rebounds from the inner surface of this sphere according to the laws of collision of perfectly elastic bodies, maintains its absolute velocity during the course of several free paths, and then changes velocity as a result of a non-symmetric action of the surrounding atoms.

Let us seek to find, under this hypothesis, what will be the most probable trajectories of the atom inside its displacement sphere. Let us assume that, for the initial position of the atom, all possible distances from the equilibrium position are equally probable; then the probability that this distance is contained between the limits r and $r + dr$ will be given by

$$\frac{dr}{\rho}. \quad (1)$$

Let us take the radius ON (*fig. 1*) of the sphere passing through the initial position M of the atom as the polar axis. Let us denote by φ the angle NMP that the direction of motion of the atom makes with this axis. Let us assume, as is done in the theory of gases, that all directions are equally probable. Then the probability that φ is contained between the limits φ and $\varphi + d\varphi$ will be

$$\frac{1}{2} \sin \varphi d\varphi.$$

Let us call δ the angle of incidence MPO . This angle is related to φ by the relation

$$r \sin \varphi = \rho \sin \delta.$$

Since the same value δ corresponds to the values δ and $\pi - \delta$ of the angle δ , the probability that an atom whose initial distance from the center of its sphere is between r and $r + dr$ meets the spherical surface at an angle of incidence between δ and $\delta + d\delta$ is given by the expression

$$\sin \varphi d\varphi = \frac{\rho^2}{r^2} \frac{\sin \delta \cos \delta d\delta}{\sqrt{1 - \frac{\rho^2}{r^2} \sin^2 \delta}}. \quad (2)$$

[Fig. 1] (*Diagram showing a sphere with center O , a point M inside the sphere, the radius ON through M , and a point P on the sphere surface, with angles φ and δ marked.*)

One obtains the same probability for any atom by multiplying this expression by dr/ρ and extending the sum over all values of r possible for a given δ , that is, by integrating with respect to r between the limits $\rho \sin \delta$ and ρ ,

$$\varpi_\delta = \int_{\rho \sin \delta}^{\rho} \frac{\rho}{r^2} \frac{\sin \delta \cos \delta d\delta}{\sqrt{1 - \frac{\rho^2}{r^2} \sin^2 \delta}} dr = \left(\frac{\pi}{2} - \delta \right) \cos \delta d\delta. \quad (3)$$

It is evident that this probability has a maximum for $\delta = 0$. This means that motions along the diameters of the displacement spheres are the most probable. It will most often happen that between two neighboring perturbations each atom will trace trajectories deviating little from the stellar form (*fig. 2*).

[Fig. 2] (*Diagram showing a star-shaped trajectory pattern inside a circle.*)

If we suppose that each periodic change in the motion of an atom produces a wave of the same period in the surrounding ether, and if we consider that the

waves produced by the radial motions indicated above will be not only the most frequent, but also the most intense, we can admit, as a first approximation, that it is these motions alone that determine the composition of the radiations emitted by our solid.

But the period of vibration corresponding to this radial motion is evidently related to the instantaneous velocity v of the atom by the relation

$$\tau = \frac{4\rho}{v}. \quad (4)$$

This relation can be used for the transformation of the well-known formula of Maxwell, which expresses the most probable distribution of kinetic energies among a large number of arbitrary material points continuously exchanging their velocities by means of forces having a potential ⁽¹⁾. If we denote by N the total number of atoms, by m the mass of each of them, by e the base of Napierian logarithms, by $k = 3/(2m\bar{v}^2)$ a constant inversely proportional to the mean kinetic energy $(m\bar{v}^2)/2$ of an atom, the law of Maxwell gives the number of atoms whose velocities will be contained between the limits v and $v + dv$; this number is

$$\nu_v = \frac{4N}{\sqrt{\pi}} (km)^{3/2} e^{-kmv^2} v^2 dv. \quad (5)$$

⁽¹⁾ See on this subject: L. Boltzmann, *Ueber die Beziehung zwischen dem zweiten Hauptsatze der mechanischen Wärmetheorie und der Wahrscheinlichkeitsrechnung*, etc. (*Sitzungsber. der Wiener Akad. der Wiss.*, vol. LXXVI, pp. 373–435, October 1877); as well as Watson, *A Treatise on the Kinetic Theory of Gases*. Oxford, 1876, p. 12, etc.

Replacing, according to (4), v by $4/\tau$, we obtain

$$\nu_\tau = \frac{256N}{\sqrt{\pi}} \rho^3 (km)^{3/2} e^{-\frac{16km\rho^2}{\tau^2}} \tau^{-4} d\tau. \quad (6)$$

This formula gives the number of atoms whose principal periods of vibration are between the limits τ and $\tau + d\tau$. This is the probable law of the distribution of vibration durations among the atoms of our solid.

Because of the law of superposition of vibratory motions, one can admit that the intensity of a simple radiation of duration τ must be:

1° Proportional to the number ν_τ of atoms of the radiating source vibrating in the same period;

2° Proportional to a function of the kinetic energy of these same atoms. Because of the relation (4) and the large value of $1/\tau$ for all the radiations we shall have to consider, this function can be reduced to a power of $1/\tau^2$;

3° Finally, directly proportional to an unknown function of the absolute temperature of the body. This function constitutes a factor that must represent the mean reinforcement or weakening caused to each primitive wave by the totality of the resultant vibrations ⁽¹⁾ and by absorption in the radiating body itself. We shall denote this function by $f(T)$.

⁽¹⁾ These are the resultant waves which, according to the analysis of Mr. Helmholtz, must form whenever the square of the elongation is not negligible. They explain, according to this author, the phenomenon of combination tones (Combinationstöne). In the case we are considering, they must form especially at the surface of the radiating body, since the forces that restore the atoms to their equilibrium positions are not symmetric in all directions there.

Thus, denoting by A and p positive constants, we set the intensity of the simple ethereal undulation of period τ as

$$I_\tau = A \nu_\tau \left(\frac{1}{\tau^2} \right)^p f(T). \quad (7)$$

Considering, as usual, the absolute temperature T as proportional to the mean kinetic energy of an atom, we can replace in formula (6) the constant k by M/T , where M is independent of T . Then introducing this expression (6) into equation (7), and setting, for brevity,

$$A \frac{256N}{\sqrt{\pi}} \rho^3 (Mm)^{3/2} = B, \quad 16\rho^2 Mm = c, \quad (8)$$

we shall have

$$I_\tau = B T^{-3/2} f(T) e^{-\frac{c}{T\tau^2}} \tau^{-(2p+4)} d\tau. \quad (9)$$

Let us now replace the variable τ by the variable $\lambda = V/\tau$, where λ is the ethereal wavelength and V is the speed of propagation of light. After this, still denoting the constant coefficients appropriately modified by B and c , we shall have

$$I_\lambda d\lambda = B T^{-3/2} f(T) e^{-\frac{c}{T\lambda^2}} \lambda^{-(2p+4)} d\lambda. \quad (10)$$

This formula gives the intensity of a simple radiation of wavelength λ as a function of this wavelength and the absolute temperature of the source.

It is toward a law of this kind that the distribution of radiant energy in each spectrum must tend, as its continuity becomes more and more perfect, that is to say, as the condensation of the source increases and the selective absorptions along the path of the rays are diminished. To have a more complete law, it would still be necessary to determine the value of p and the form of $f(T)$; but

our formula will give some interesting results, even without our needing to make such a specialization.

It is evident that, in this general form, our law embraces, as particular cases, all the empirical emission laws proposed up to now, such as the laws of Newton, of Dulong and Petit, and of Mr. Stefan.

If we assign to T a constant value and take λ as abscissa, I_λ as ordinate, equation (10) will be that of the energy curve in the continuous normal spectrum of a solid source at temperature T . These are the curves that Mr. Crova has called *isothermic curves* ⁽¹⁾. To study the general properties of these curves, I take the derivative of the expression I_λ , assuming T to be constant.

⁽¹⁾ A. Crova, *Study of Radiations*, etc. (*Ann. de Chim. et de Phys.*, [5], vol. XIX, p. 472).

2. Limits of the Spectrum

It is easy to see, from formula (10) and its derivative, that if $f(T)$ and T have finite values, one will always have for $\lambda = 0$ and $\lambda = \infty$

$$I_\lambda = 0 \quad \text{and} \quad \frac{dI_\lambda}{d\lambda} = 0.$$

This means that all the energy curves represented by equation (10) are tangent to the λ -axis at the origin of coordinates, and that they have this axis as an asymptote. At both extremities of the spectrum, the radiant energy diminishes to zero; but, while toward the violet end the vanishing is almost sudden, because of the rapid decrease of the factor $e^{-c/(T^2)}$, the less refrangible energy extends indefinitely toward the side of increasing λ . This fact has been observed recently by Mr. Langley ⁽²⁾.

⁽²⁾ S.-P. Langley, *On Invisible Spectra* (*Ann. de Chim. et de Phys.*, Dec. 1886.)

3. Maximum of Intensity

Each of the curves represented by equation (10) presents only a single maximum defined by the condition

$$\lambda_{\max} = \sqrt{\frac{c}{p+2}} \cdot \frac{1}{\sqrt{T}}. \quad (11)$$

One sees that the position of maximum intensity in our spectra depends on the temperature, and formula (11) gives the law of this dependence: **Whatever the law of emission, the wavelength corresponding to the maximum**

energy is inversely proportional to the square root of the absolute temperature of the source.

The only experimental measurements, to my knowledge, that have been published so far on this subject are contained in a recent diagram by Mr. Langley ⁽¹⁾. To compare this data with the relation $T_{\text{max}}^2 = \text{const.}$, equivalent to (11), I have drawn from this diagram, by a graphical method, the following values of T_{max} :

Temperatures			
°C	T	T_{max} ()	T_{max}^2
178	451	4.90	10828
330	603	4.05	9891
525	798	3.63	10515
815	1088	3.27	11634

Although the constancy of T_{max}^2 is far from perfect, nevertheless, considering the manner in which these four values were obtained and the uncertainty in the estimation of high temperatures, one can say that the observations appear to confirm our theory.

⁽¹⁾ *Loc. cit.*, p. 462.

4. Measurement of Temperatures

Supposing that this law is justified by more numerous experiments, it will furnish us a very simple method for measuring the high temperatures of radiating bodies ⁽²⁾. This method would be superior to the spectro-photometric method developed by Mr. Crova, in that it would not depend on the choice of compared tints and would give not optical degrees, but absolute temperatures.

⁽²⁾ The idea of a similar method, however without any definite law, was stated by Mr. Crova, *loc. cit.*, p. 479.

Knowing the constant of equation (11), it would suffice, in order to determine the temperature of an incandescent body, to measure the wavelength corresponding to the maximum intensity of its normal spectrum.

If one takes into account as much as possible the absorptions suffered by solar rays and one admits that the considerable density and enormous mass of the Sun must give to its primitive spectrum all the qualities of continuous spectra, one can apply this method to the calculation of the temperature of the Sun. According to the observations of Mr. Langley ⁽¹⁾, the maximum of intensity in the solar spectrum observed beyond our atmosphere would be situated near $\lambda = 0.5 \mu$. Therefore, if, according to the preceding Table, one takes in round

numbers $T^2_{\text{max}} = 10000$, one obtains for the absolute temperature of the Sun approximately $40,000^\circ$. It must be noted that this method assumes only an analogy in the distribution of energy in the primitive spectrum of the Sun and that of lampblack, while the total emissive power may be quite different for these two bodies.

(¹) S.-P. Langley, *Researches on Solar Heat, a Report of the Mount Whitney Expedition*, p. 144, Pl. XV, curve III. Washington, 1884.

5. Total Radiant Energy

By calculating the area of each curve represented by equation (10), I obtain the total radiant energy of the spectrum

$$E = \int_0^\infty I_\lambda d\lambda = \frac{1}{2} B c^{-(p+3/2)} \Gamma\left(p + \frac{3}{2}\right) f(T) T^p, \quad (12)$$

where Γ denotes the Eulerian integral of the second kind (the Gamma function).

Let us compare this formula with the one obtained by eliminating between equations (10) and (11), that is, with the maximum intensity of the spectrum

$$I_{\text{max}} = B \left(\frac{p+2}{ec} \right)^{p+2} f(T)^{p+1/2}. \quad (13)$$

Apart from constant coefficients, expressions (12) and (13) differ only in that the second contains an additional factor $\sqrt{T}$. Therefore the maximum intensity increases with temperature more rapidly than the total radiant energy, and their ratio

$$\frac{I_{\text{max}}}{E} = \frac{2 c^{-1/2}}{\Gamma(p + \frac{3}{2})} \left(\frac{p+2}{e} \right)^{p+2} \sqrt{T} \quad (14)$$

increases in direct proportion to the square root of the absolute temperature of the source.

Multiplying equations (11) and (14), one obtains

$$\frac{I_{\text{max}} \lambda_{\text{max}}}{E} = \frac{2 e^{-(p+2)}}{\Gamma(p + \frac{3}{2})} (p+2)^{p+3/2} = \text{const.} \quad (15)$$

This interesting relation shows that **the total radiant energy emitted by a solid is in a constant ratio to the product of the maximum energy of the normal spectrum by the corresponding wavelength**, or, in other

words, that the area of each energy curve is in direct proportion to the area of the rectangle having as sides the coordinates of the summit of this curve (see below, *fig. 3*). This constant ratio depends only on the value of p which, probably, is the same for all bodies; for, in our equations, it is this value that characterizes the mode of action between the ponderable atoms and the surrounding ether.

This relation, which does not at all require knowledge of the temperature, would lend itself better to experimental verification than the preceding relations. For the moment, there are no direct data to make such a verification. It is only in a very imperfect manner that I was able to extract, by measuring the ordinates and areas of Mr. Langley's traces, the following relative values of I_{max} and E .

T	λ_{max} ()	I_{max}	E	$I_{\text{max}} \cdot \lambda_{\text{max}} / E$
451	4.90	5.2	182	0.140
603	4.05	21.5	532	0.163
798	3.63	39.7	1074	0.134
1088	3.27	64.9	1730	0.123

Given the imperfection of the verification procedure, the numbers in the last column, which should be equal according to our theory, are not too unfavorable to it.

6. Plotting the Curves

To be able to plot the energy curves, it is necessary to give special values to p and to $f(T)$. If, for example, one admits with Mr. Stefan ⁽¹⁾ that the radiant energy emitted by a body is directly proportional to the fourth power of its absolute temperature, one can set

$$p = 1, \quad f(T) = KT^3,$$

after which equation (10) will take the form

$$I_{\lambda} = B_1 T^{3/2} e^{-\frac{c}{T\lambda^2}} \lambda^{-6}. \quad (16)$$

Having determined the two constants B and c of this equation from a diagram of the invisible normal spectrum of lampblack at 178°C, given by Mr. Langley ⁽²⁾, I calculated and plotted the theoretical curves (16) for this temperature and for 327°C = 600° abs. (*fig. 3*).

⁽¹⁾ Stefan, *Sitzungsber. der Wien. Akad.*, vol. LXXIX, p. 391; 1879. ⁽²⁾ *Ann. de Chim. et de Phys.*, Dec. 1886, p. 439, fig. 1, and *Phil. Mag.*, vol. XXII, Pl. IV.

[**Fig. 3**] (*Diagram showing two asymmetric energy curves at 178°C and 327°C, with wavelength on the horizontal axis (0 to 14 μ) and intensity on the vertical axis. The curves show the characteristic features described in the text.*)

One sees that these curves have all the qualities that Mr. Langley attributes ⁽³⁾ to the curves obtained experimentally, namely:

1° The radiant energy, represented by the ordinates, while diminishing on both sides, extends indefinitely toward the side of less refrangible waves.

2° When the temperature increases, all ordinates grow, but in unequal proportions: those representing the energy of more refrangible waves always increase more rapidly than those corresponding to longer undulations.

3° Hence the independently observed fact that the maximum ordinate progressively shifts toward the more refrangible region. Above, we have indicated the probable law of this displacement.

4° The theoretical curves of the normal spectrum, as well as the prismatic curves of Mr. Langley, are not symmetric: the greater part of their areas lies to the right of the maximum ordinate, that is, on the side of less refrangible waves.

5° In accordance with this, the fall of each curve is more rapid on the side of shorter undulations. For the two cases for which we give diagrams, all sensible heat disappears before the curves have reached the limits of the visible spectrum; there are only obscure heats.

⁽³⁾ *Ibid.*, pp. 471–472, and *Phil. Mag.*, vol. XXI, pp. 403–404.

7. Solar Curve

I have also tried to compare my theoretical curves, as to their general form, with the curve of solar energy beyond the atmosphere. In *fig. 4*, the separate points correspond to the numbers given by Mr. Langley, in no. 9 of table 120 of his work: *Researches on Solar Heat*, etc.; the dotted curve has been traced after curve III of Plate XV of the same Work, and the solid line gives the theoretical curve represented by the equation

$$I_{\lambda} = A e^{-\frac{M}{\lambda^2}} \lambda^{-6}, \quad (17)$$

and passing through the two observed points A and B.

[**Fig. 4**] (*Diagram showing the solar energy curve with wavelength on the horizontal axis (0.2 to 1.8 μ). Points I, II, III mark observed data, a dotted curve shows Langley's data, and a solid curve shows the theoretical fit through points A and B.*)

To account for the difference between theory and observation (a difference more considerable this time than in the preceding case), let us recall: 1° that not only equation (17), but also the more general formula (10), can only be considered as a first approximation; 2° that these formulas have been derived for solids and not for bodies such as the Sun; and finally 3° that, in our atmosphere as well as in the cooler regions of the gases surrounding the Sun, the phenomenon of the *degradation* of radiant energy must occur. Thanks to this effect, which has not been eliminated by Mr. Langley, a portion of the more refrangible radiations must be transformed into longer undulations, which will tend to modify the spectral diagram precisely in the direction indicated by observation.

While recognizing the provisional character of the ideas sketched in this article, I hope that it will be possible to give them more development and precision, once we are in possession of more complete experimental data that will be able to guide us in this study. One will then be able to express by a sufficiently exact formula the law of the distribution of radiant energy as a function of wavelength and temperature of the source. Such a formula will be of great utility in all questions relating to the study of spectra.